BIODEGRADABLE DETERGENTS

LOUIS LONG, JR., CLAUDE H. TROTTIER, FIRST LIEUTENANT,
CHEMICAL CORPS, MORRIS R. ROGERS, AND ARTHUR M. KAPLAN

U. S. ARMY NATICK LABORATORIES
NATICK, MASSACHUSETTS

Synthetic detergents have had a spectacular success since
their commercial introduction thirty years ago, current annual
production amounting to some 700 million pounds. The United
States Army alone purchases detergents worth millions of dollars
each year. Recently, their biodegradability has become the sub-
ject of concern, chiefly due to legislation enacted in West Germany
which stipulates that anionic detergents must be at least 80 per cent
biodegradable (1). Two bills have been introduced in Congress
aiming at a ban on selling and importing detergents which do not
decompose quickly and completely, and pertinent legislation has
been considered in a number of states (2).

Within the past year, industry has converted from branched
chain detergents (ABS), Fig. 1, to straight-chain detergents (LAS),
Fig. 2, in the hope that the persistent foams that now form on water-
ways, sewage-treatment plants and in drinking water will be eliminat-
ed. There is, however, evidence that increased biodegradability
may become necessary; the introduction of a third "generation" of
detergents may be required (3). This paper provides insight into
the mechanism of degradation and reports the synthesis of new and
more biodegradable detergents.

The search for improved biodegradable detergents has
shown that sodium p-(n-dodecyl)benzenesulfonate is the most
rapidly degraded of the various isomers of sodium dodecylbenzene-
sulfonate (4). The elimination of branched alkyl groups in the ABS
molecule causes a pronounced increase in the biodegradation. The
position of the phenyl group also has an effect on the degradation,
which increases as the phenyl group moves toward the end of the

chain (5), Fig. 3. An additional factor is the position of the sulfonate group in the benzene ring. The para substituted compound degrades more readily than the ortho, Fig. 4.

We have attempted to improve the biodegradability of the straight-chain anionic detergents by a novel approach involving the synthesis of the thia derivatives of sodium p-(n-dodecyl)benzenesulfonate in which the different methylene groups are successively replaced by sulfur. The eleven possible isomers of sodium p-(thia-n-dodecyl)benzenesulfonate, Fig. 5, were first synthesized in our laboratory. The sulfur atoms were also oxidized to sulfoxides, forming another series of compounds containing the sulfinyl group, Fig. 6.

EXPERIMENTAL

Material

Apparatus. The nuclear magnetic resonance spectra were recorded on a Varian 60 Mc spectrometer at 60°. The samples were dissolved in deuterated water with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal standard ($\tau = 10.00$ for the trimethylsilyl protons). The infrared spectra were recorded on a Beckman IR 9 spectrophotometer using KBr-pellets. Temperature measurements are uncorrected.

Sodium p-(1-Thia-n-dodecyl)benzenesulfonate. Sodium (11.5 g., 0.50 mole) was dissolved in 250 ml. of absolute ethanol and 55 g. of thiophenol (0.50 mole) was added. Under external cooling, 95 g. of n-undecyl chloride (0.50 mole) was added and the reaction mixture was boiled under reflux for 3.5 hr. The precipitated sodium chloride was filtered, the solvent evaporated, and the residue dissolved in a mixture of petroleum ether and benzene, from which the phenyl-n-undecyl sulfide crystallized on cooling. Yield 102 g. (0.39 mole, 77%); mp 31-33° (lit. (6) mp 33.8°).

A solution of 20 g. (0.08 mole) of phenyl n-undecyl sulfide in 10 ml. of chloroform was dropped during 1 hr. into 30 ml. (0.45 mole) of chlorosulfonic acid with stirring at 25°. The reaction mixture was poured on ice and the organic material extracted with ether. The ether solution was washed with water, sodium bicarbonate solution, again with water, and dried. Evaporation of the solvent yielded 18 g. (0.05 mole, 65%) of crude p-(1-thia-n-dodecyl)benzenesulfonyl chloride. Its infrared spectrum showed the typical absorption bands for the sulfonyl chloride group at 1175 and 1370 cm^{-1}. In 150 ml. of 60% ethanol, 4.0 g. (0.10 mole)

of sodium hydroxide and 18 g. (0.05 mole) of the sulfonyl chloride
were dissolved, and the mixture was stirred for several hours at
room temperature. On cooling the solution in an ice-bath, sodium
p-(1-thia-n-dodecyl)benzenesulfonate crystallized in colorless leaf-
lets. After three recrystallizations from 50% ethanol, 12 g.
(0.03 mole, 65%) was obtained.

Anal. Calc. for $C_{17}H_{27}O_3S_2Na$ (366.53); C, 55.71; H, 7.43;
S, 17.50. Found: C, 55.91; H, 7.46; S, 17.61.

Sodium p-(2-Thia-n-dodecyl)benzenesulfonate. The pro-
cedure for preparing sodium α-chloro-p-toluenesulfonate (7) was
adapted to a bench-scale method. Sodium p-toluenesulfonate (68 g.,
0.35 mole) was placed in a 500-ml. four-necked flask provided with
a mechanical stirrer, a thermometer, and a gas-inlet and outlet.
The flask was immersed in an oil-bath at 120°, and, with stirring
of the dry salt, chlorine was passed in. The internal temperature
rose to 145°. After 75 min., the reactant had gained 11 g. The
crude reaction product was twice recrystallized from 90% ethanol.
The analysis as well as the nuclear magnetic resonance (NMR)
spectrum indicated that it was a mixture of mono- and dichlorinated
toluenesulfonate. Its NMR spectrum in deuterated water (TMS as an
external standard) showed, beside the signals for the phenyl protons
around τ 2.4 and the singlet for the benzyl protons at τ 5.37, another
singlet at τ 3.04 due to the benzal proton. From the intensities of
the signals the proportion of the compounds was calculated to be
about 60% α-monochloro- and 40% α-dichlorotoluenesulfonate.

To a solution of 26 g. of this mixture (about 0.10 mole)
and 6.0 g. (0.15 mole) of sodium hydroxide, 400 ml. of 40%
ethanol and 26 g. (0.15 mole) of n-decanethiol were added, and the
reaction mixture was boiled under reflux for 2 hr. After neutraliza-
tion with hydrochloric acid, the solution was cooled, and the pre-
cipitated colorless leaflets of sodium p-(2-thia-n-dodecyl)-benzene-
sulfonate were recrystallized three times from 50% ethanol. Yield
18 g. (0.05 mole, approximately 50%).

Anal. Calc. for $C_{17}H_{27}O_3S_2Na$ (366.53); C, 55.71; H, 7.43;
S, 17.50. Found: C, 55.76; H, 7.47; S, 17.38.

General Procedure for the Synthesis of Sodium p-(N-Thia-
n-dodecyl)-benzenesulfonates for N = 3 to 11 inclusive. The chloro-
alkylbenzene (1.0 mole) was added dropwise during 1.5 hr. to
chlorosulfonic acid (10.0 moles) with efficient stirring, and
external cooling by a water bath at temperatures between 0 and 25°.

The reaction mixture was stirred for another hour and then poured onto ice. The aqueous mixture was extracted with ether; the ether layer was separated from the water layer, and the ether removed by evaporation in vacuum. The residue was purified by distillation under reduced pressure.

In the case of p-(2-chloroethyl)benzenesulfonyl chloride, the aqueous insoluble product was crystalline. It was purified by two recrystallizations from a mixture of petroleum ether and ether (3:1). Yield 27 g. (0.11 mole, 57%); mp 53.5-55°.

Anal. Calc for $C_8H_8Cl_2O_2S$(239.13); C, 40.18; H, 3.37; Cl 29.65; S, 13.41. Found: C, 40.32; H, 3.50; Cl, 29.58; S, 13.30.

The infrared spectrum of this product (potassium bromide) exhibits strong bands at 1180 and 1380 cm^{-1} due to the sulfonyl chloride group and weak bands at 1800 and 1925 cm^{-1} that indicate a 1,4-disubstituted benzene.

The purified chloroalkylbenzenesulfonyl chloride (1.0 mole) was added to a solution of sodium hydroxide (2.0 moles) in water (5.9 ml. of water per gram of sodium hydroxide), and the heterogeneous reaction mixture was stirred vigorously until it became homogeneous. The solution was neutralized with hydrochloric acid and evaporated to dryness. Recrystallization of the residue from ethanol yielded crystalline sodium p-(chloroalkyl)benzenesulfonate.

A mixture of equimolecular quantities of sodium p-(chloroalkyl) benzenesulfonate, sodium hydroxide and n-alkylmercaptan was boiled under reflux for 3 hr. On cooling the solution, the desired product crystallized. Recrystallization from water, or aqueous ethanol, afforded pure crystalline sodium p-(N-thia-n-dodecyl)benzenesulfonate in yields of from 20 to 65%, Table I.

General Procedure for the Synthesis of Sodium p-(N-sulfinyl-n-dodecyl)benzene sulfonates. The sodium p-(N-thia-n-dodecyl)benzene sulfonate (1.0 mole) dissolved in 50 ml. of water was slowly added to a solution of sodium metaperiodate (1.1 mole) in 100 ml. water and 50 ml. of dioxane at 0°. The reaction mixture was stirred for 24 hr. at room temperature and the solvent removed by evaporation in vacuum. The crude product was purified by recrystallization from ethanol and ethanol-water, Table II.

General Procedures for the Biodegradability Tests. River Die-Away Test (8). A twenty milligram sample of surfactant was

LONG, TROTTIER,

ROGERS and KAPLAN

dissolved in one-half liter of Sudbury River water. The contents were mixed and the liquid incubated at rest. The contents were mixed for one minute prior to sample withdrawal, and the samples analyzed by the standard methylene blue method (9).

Shake Flask Method (8). A mixed microbial culture, referred to as "the laboratory culture," originating from waste treatment plant activated sludge, was used for all shake flask degradation studies. The surfactant solution (20-30 mg./1) was measured into a shake flask and the sample sterilized in an autoclave at 20 psig for twenty minutes. After sterilization and cooling, the flask was innoculated with 10 ml./liter of an adapted 72 hour mixed microbial culture. The liquid was then incubated on a reciprocating shaker at 25°.

DISCUSSION AND RESULTS

A possible mechanism for the biodegradation of the LAS molecule in aqueous solution involves, as a first step, the oxidation of the terminal methyl group to a carboxylic acid. In this process, a primary hydroperoxide is formed, followed by reactions which convert the hydroperoxide to a primary alcohol, an aldehyde and finally a carboxylic acid (10), Fig. 7.

In a second step, beta oxidation of the carboxylic acid can occur after its esterification by coenzyme A (11). Subsequently, two protons are removed to form an α,β-unsaturated compound, which may be hydrated to a β-hydroxyl compound and dehydrogenated to a β-keto derivative. Another molecule of coenzyme A then adds between the α and β-carbon atoms, splitting off acetyl coenzyme A and leaving a fatty acid coenzyme A ester two carbons shorter than the original, ready to participate in a similar sequence of reactions for further degradation, Fig. 8.

As a final step, the phenyl group can be ruptured by an oxidative mechanism in which catechol is formed by an enzyme catalyzed oxidation with molecular oxygen (12). Ring opening to a dicarboxylic acid then occurs followed by three successive molecular rearrangements to form β-keto adipic acid which could thereafter undergo a β-oxidation process to afford acetate and succinate groups, both of which are cell metabolites, Fig. 9.

Such a mechanism, however, does not explain the degradation of the branched chain benzene sulfonates (ABS) which are decomposed by bacteria, though at a slower rate. It is assumed that branching in the alkyl chain inhibits the β-oxidation mechanism.

An alternate mechanism might be attack at an intermediate point in
the alkyl chain with subsequent rupture. Since the biological fission
of a carbon-sulfur bond has been shown to occur in a number of
cases (13), the synthesis of compounds with a sulfur atom in the
side-chain was undertaken. Such detergents should be more bio-
degradable than LAS and should have physical properties similar to
those of LAS compounds as the configuration of a sulfur atom is
closely analogous to that of a methylene group. Furthermore, since
biodegradation presumably proceeds by way of oxidation, the sulfur
atom in the side-chain might be first oxidized to a sulfoxide. Syn-
thesis of a series of sodium p-(sulfinyl-n-dodecy'.)benzenesulfonates
was therefore undertaken to determine the role of a sulfoxide group
in the biodegradation.

Preliminary results concerning the biodegradability of
sulfinyl compounds indicate that they are less biodegradable than
the "thia" compounds.

As a result, it may be assumed that the mechanism of bio-
degradation of the sodium p-(thia-n-dodecyl)benzenesulfonates is
not initial oxidation to a sulfoxide with subsequent rupture of the
carbon-sulfur bond. Rather the presence of a sulfoxide group
probably has an adverse effect on the biodegradation of the molecule
indicating that some other mode of biodegradation is preferred.

Four isomers of sodium p-(N-thia-n-dodecyl)benzene-
sulfonate (N= 1, 2, 3, and 4) have proved to be better than the com-
mercial standard (14) in tests for biodegradability by the shake
flask method. They were completely biodegraded in two days as
compared to three days for the standard. Biodegradation, there-
fore, increases as the position of the sulfur atom in the side-chain
approaches the benzene ring.

CONCLUSION
The incorporation of a sulfur atom into the alkyl side-chain
of the LAS molecule has provided insight into the mechanism of its
biodegradation and has resulted in the synthesis of new and more
biodegradable detergents. The introduction of other heteroatoms
into the side-chain of the LAS molecule should achieve further
improvements in its biodegradability.

LONG, TROTTIER,
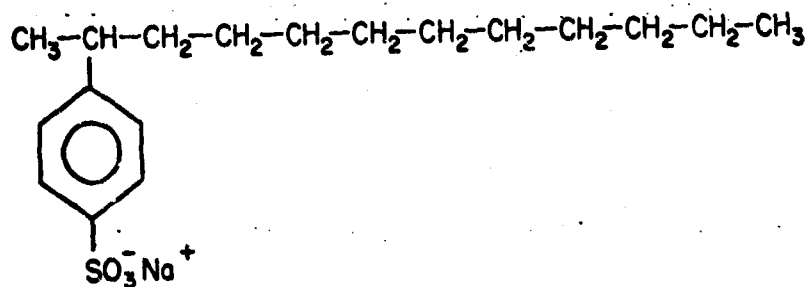ROGERS and KAPLAN

LITERATURE CITED

1. Chem. and Eng. News, 41, No. 7, 65 (1963).
2. Soap and Chemical Specialties, 39, No. 6, 59 (1963).
3. E. A. Knaggs, "The Detergent Dilemma," Int'l Science and
    Technology, No. 41, 27 (1965).
4. R. D. Swisher, J. Water Pollution Control Federation, 35 (7),
    877 (1963).
5. R. D. Swisher, J. Am. Oil Chem. Soc., 40, 648 (1963).
6. S. O. Jones and E. E. Reid, J. Am. Chem. Soc., 60, 2452
    (1938).
7. Gessellschaft für Chemische Industrie in Basel, Basel,
    Switzerland, D.R.P. 312959 (21 June 1919); Chem.
    Zentr., 1919, IV, 373; FRDL, 13, 220
8. Continental Oil Co. Technical Bull. 54-500-964.
9. J. C. Vaughn, J. Am. Water Works Assoc., 50, No. 10, 1343
    (1958).
10. R. E. Kallio and J. E. Stewart, J. Bacteriol., 78, 441 (1959).
11. P. K. Stumpf and G. A. Barber, "Comparative Mechanisms
    for Fatty Acid Oxidation," Comparative Biochemistry,
    Florkin and Mason, Ed., Academic Press, New York,
    N.Y., 1960, pp. 75-100.
12. W. E. Knox, "Degradation of Aromatic Compounds," Bio-
    chemists' Handbook, Van Nostrand, New York, N.Y.,
    1961, pp. 596-601.
13. F. Challenger and P. T. Charlton, J. Chem. Soc., 424(1947);
    F. Binkley, J. Biol. Chem., 186, 287 (1950);
    V. Du Vigneaud, "A Trail of Research," Cornell
    University Press, Ithaca, New York (1952); F. Challenger,
    Endeavour, 12, 177 (1953).
14. Sample obtained from the Soap and Detergent Association,
    295 Madison Avenue, New York, N.Y.
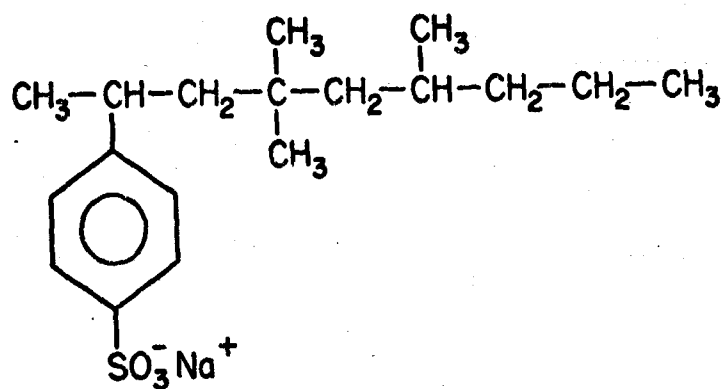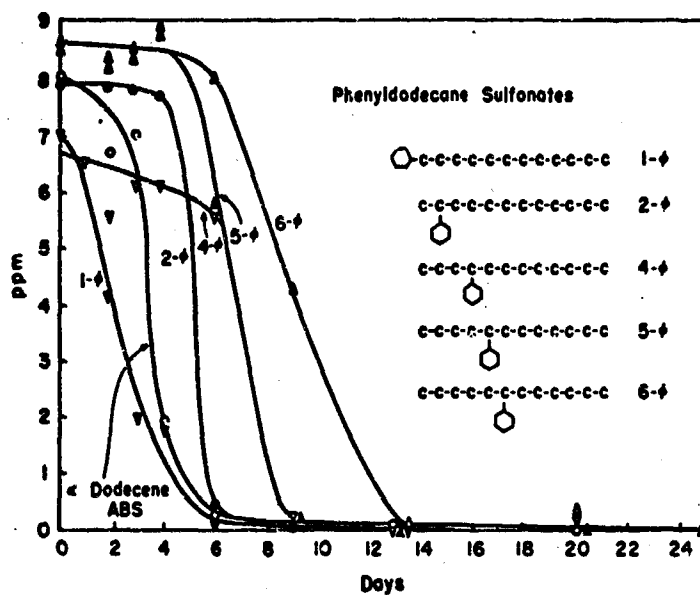
Example of Branched-Chain Detergent (ABS).

Fig. 1

Example of Straight-Chain Detergent (LAS).

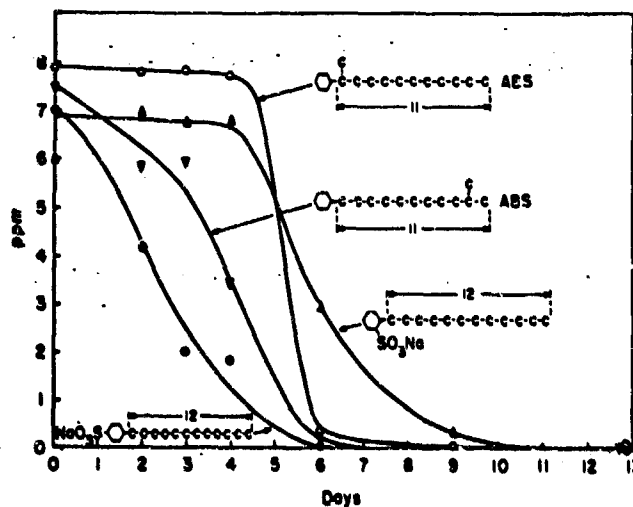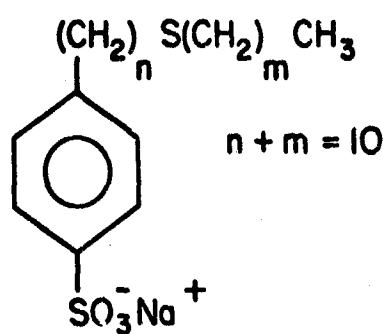Fig. 2

Disappearance curves for phenyldodecane ABS isomers.

Fig. 3

Disappearance curves of the 1-phenyldodecane ortho and
para sulfonates; methyi branched ABS.
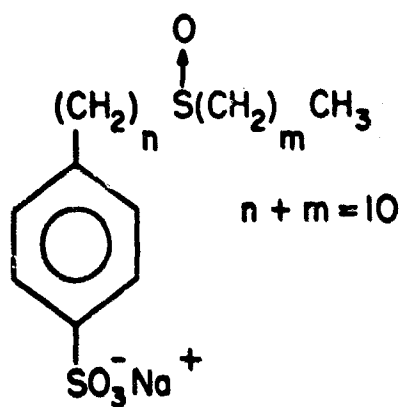
Fig. 4

$(CH_2)_n S(CH_2)_m CH_3$

$n + m = 10$

$SO_3^- Na^+$

Sodium p-(Thia-n-dodecyl) benzenesulfonate.

Fig. 5

O

$(CH_2)_n \overset{O}{S}(CH_2)_m CH_3$

$n + m = 10$

$SO_3^- Na^+$

Sodium p-(Sulfinyl-n-dodecyl) benzenesulfonate.

Fig. 6

R-CH$_2$-CH$_2$-CH$_3$

O$_2$

R-CH$_2$-CH$_2$-CH$_2$-O·OH

R-CH$_2$-CH$_2$-CH$_2$-OH

$$R-CH_2-CH_2-\overset{O}{\overset{\|}{C}}H$$

$$R-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$$
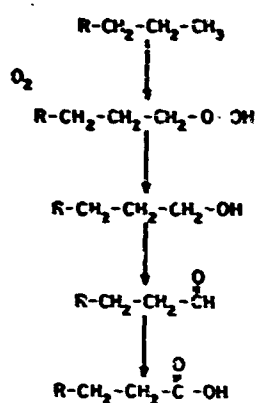
Stages in biochemical oxidation of
methyl group to carboxyl

Fig. 7

$$R-CH_2CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

HSCoA

$$R-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-SCoA \qquad +H_2O$$

$$R-CH_2-CH_2-CH=CH-\overset{O}{\overset{\|}{C}}-SCoA \qquad (+2H)$$

H$_2$O

$$R-CH_2-CH_2-\overset{OH}{\underset{}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-SCoA$$

$$R-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-SCoA \qquad (+2H)$$

HSCoA

$$R-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-SCoA \qquad +CH_2-\overset{O}{\overset{\|}{C}}-SCoA$$
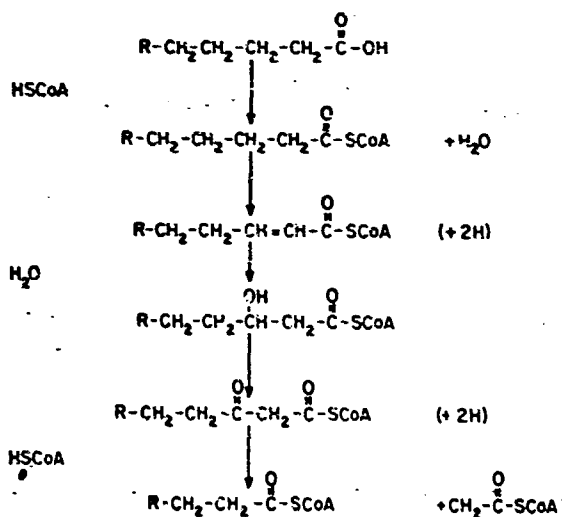
Stages in beta oxidation (HSCoA = coenzyme A).

Fig. 8
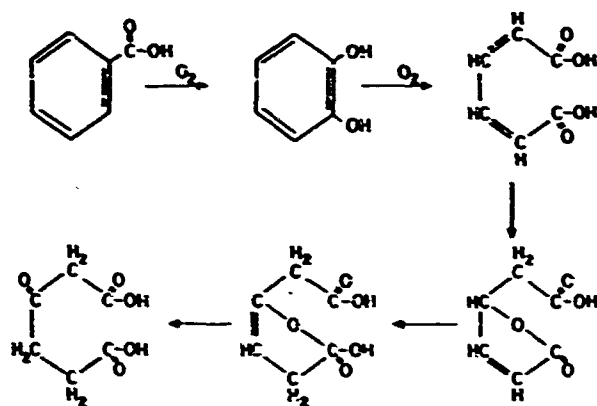
Stages in biochemical oxidation of aromatic ring

Fig. 9

TABLE I
Yields and Analyses of
Sodium p-(Thia-n-dodecyl)benzenesulfonates

Sodium p-(Thia-n-dodecyl)-benzenesulfonate	Yield %	Carbon, % (Calc. - 55.71)	Hydrogen, % (Calc. - 7.43)	Sulfur, % (Calc. - 17.50)
Sodium p-(3-thia-n-dodecyl)-benzenesulfonate	65	55.48	7.45	17.43
Sodium p-(4-thia-n-dodecyl)-benzenesulfonate	46	55.83	7.29	17.55
Sodium p-(5-thia-n-dodecyl)-benzenesulfonate	29	55.72	7.48	17.59
Sodium p-(6-thia-n-dodecyl)-benzenesulfonate	31	55.64	7.33	17.23
Sodium p-(7-thia-n-dodecyl)-benzenesulfonate	34	55.62	7.27	17.69
Sodium p-(8-thia-n-dodecyl)-benzenesulfonate	31	55.89	7.28	17.63
Sodium p-(9-thia-n-dodecyl)-benzenesulfonate	20	55.71	7.22	17.34
Sodium p-(10-thia-n-dodecyl)-benzenesulfonate	31	55.73	7.48	17.48
Sodium p-(11-thia-n-dodecyl)-benzenesulfonate	32	55.89	7.35	17.29

TABLE II
Yields and Analyses of
Sodium p-(Sulfinyl-n-dodecyl)benzenesulfonates

Sodium p-(Sulfinyl-n-dodecyl) benzenesulfonate	Yield %	Carbon, % (Calc. - 53.37)	Hydrogen, % (Calc. - 7.11)	Sulfur, % (Calc. - 16.76)
Sodium p-(1-sulfinyl-n-dodecyl)-benzenesulfonate	74	53.19	7.00	16.74
Sodium p-(2-sulfinyl-n-dodecyl)-benzenesulfonate	53	53.23	7.13	16.48
Sodium p-(3-sulfinyl-n-dodecyl)-benzenesulfonate	92	53.40	7.15	16.66
Sodium p-(4-sulfinyl-n-dodecyl)-benzenesulfonate	73	53.08	6.91	16.73
Sodium p-(5-sulfinyl-n-dodecyl)-benzenesulfonate	75	53.18	7.23	16.54
Sodium p-(6-sulfinyl-n-dodecyl)-benzenesulfonate	80	53.60	7.12	16.65
Sodium p-(7-sulfinyl-n-dodecyl)-benzenesulfonate	92	53.08	7.00	16.57
Sodium p-(8-sulfinyl-n-dodecyl)-benzenesulfonate	63	53.60	7.12	16.56
Sodium p-(9-sulfinyl-n-dodecyl)-benzenesulfonate	65	53.18	7.07	16.78
Sodium p-(10-sulfinyl-n-dodecyl)-benzenesulfonate	66	53.50	7.15	16.59
Sodium p-(11-sulfinyl-n-dodecyl)-benzenesulfonate	80	53.40	6.97	16.61